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Supporting Information for

Stable 3D neutral gallium thioantimonate frameworks decorated with transition metal complexes for tunable photocatalytic hydrogen evolution

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Characterization

Room-temperature powder X-ray diffraction (PXRD) data were carried out on a desktop diffractometer (D2 PHASER, Bruker, Germany) using Cu-Kα (λ = 1.54184 Å) radiation operated at 30 kV and 10 mA. Energy dispersive spectroscopy (EDS) analysis were performed on scanning electron microscope (SEM) equipped with energy dispersive spectroscopy detector (ZEISS EVO 18). Elemental analyses (EA) of C, H, and N were performed on VARIO EL III elemental analyzer. Thermogravimetric analysis (TGA) measurements were performed with a Shimadzu TGA-50 system under nitrogen flow with heating rate of 10 °C/min. Fourier transform infrared (FT-IR) spectral analyses were performed on a Thermo Nicolet Avatar 6700 FT-IR spectrometer with diamond/zinc selenide optics allowing the instrument to observe from 600-4000 cm^{-1}. The room-temperature UV-Vis diffusion reflectance spectra (UV-Vis DRS) and absorption spectra of power samples were recorded on a SHIMADZU UV-3600 UV-Vis-NIR spectrophotometer coupled with an integrating sphere by using $BaSO_4$ powder as the reflectance reference. The band gap of the obtained samples can be determined from the Tauc plot with $[F(R) \times h\upsilon]^2$ vs. $h\upsilon$ by extrapolating the linear region to the abscissa, where $F(R)=(1-R)^2/2R$ and R *is* the reflectivity. Measurements of the dielectric constant were carried out on crystalline-powdered samples in a Ag|sample|Ag sandwich arrangement by using a Tonghui TH2828A impedance analyzer at frequencies of 1KHz with an applied electric field of 1V.

Single crystal X-ray diffraction

The single crystal X-ray diffraction (SC-XRD) measurements on **NCF-3-Mn**, **NCF-3-Fe** and **NCF-3-Ni** were performed on a Bruker Smart CPAD area diffractometer with nitrogen-flow temperature controller using graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation at 120 K. The structure was solved by direct method using SHELXS-2014 and the refinement against all reflections of the compound was performed using SHELXL-2014.

Preparation of the working electrode

Ground **NCF-3** powder (5 mg) and $Mg(NO_3)_2 \cdot 6H_2O$ (1 mg) were firstly dispersed in isopropanol (10 mL) and the mixed solution was kept stirring for 12 h in darkness and then ultrasonicated for 15 min at room temperature. The Pt plate electrode and the indium-tin oxide

(ITO) conductive glass were acted as the anode and the cathode, respectively. Notably, the electrodeposition actual area is about 1 cm^2. The duration of electrodeposition was 30 min. The constant working voltage was set at 30 V. Finally, the prepared **NCF-3**/ITO film electrode was washed with ethanol to remove the redundant $Mg(NO_3)_2$ and isopropanol adhered to the surface.

Electrochemical measurements

The Mott-Schottky (M-S), transient photocurrent and electrochemical impedance spectroscopy (EIS) experiments were carried out on a CHI760E electrochemistry workstation in a standard three-electrode system. The sample coated ITO glass (effective area is about 1 cm^2), the saturated calomel electrode (SCE), and the Pt plate electrode were used as the working electrode, reference electrode and auxiliary electrode, respectively. The light source is a 150 W high pressure xenon lamp, located 25 cm away from the surface of the ITO working electrode. Na_2SO_4 aqueous solution (0.5 M, 100 mL) was used as the supporting electrolyte.

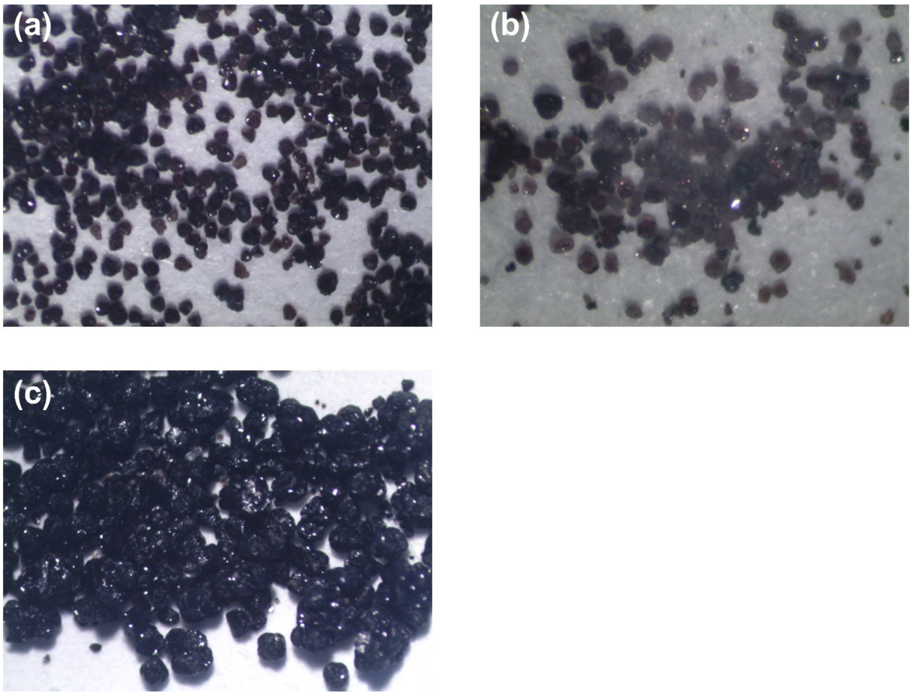

Figure S1. Photographs of the crystals of (a) **NCF-3-Mn,** (b) **NCF-3-Ni** and (c) **NCF-3-Fe**.

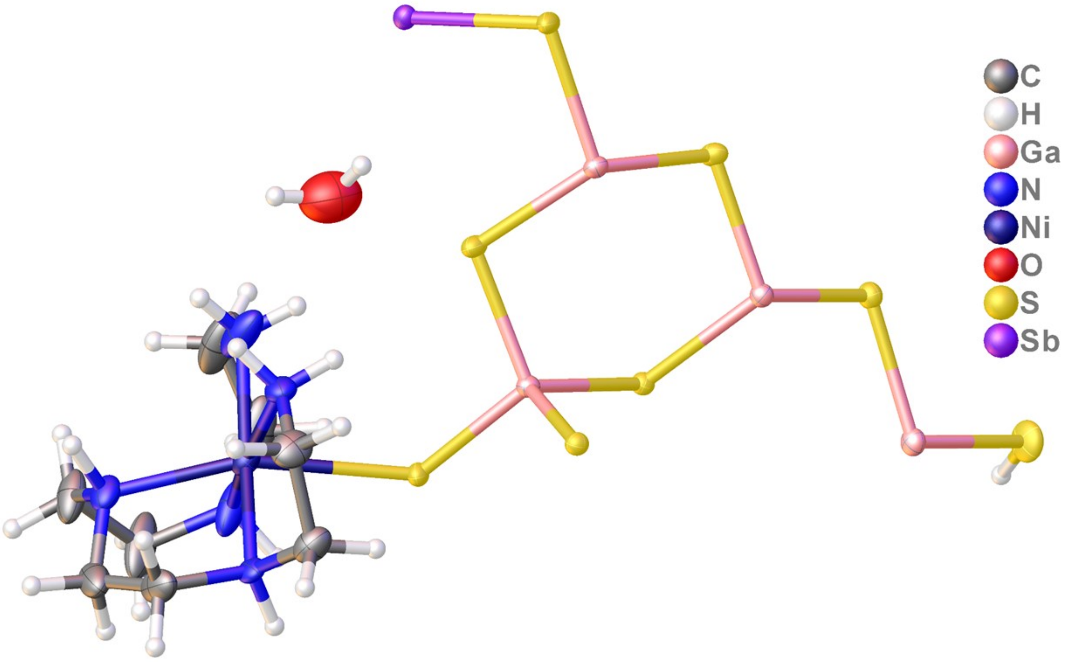

Figure S2. The asymmetric unit of **NCF-3-Ni** with 50% thermal ellipsoids shows the presence of H_2O molecules in the pores.

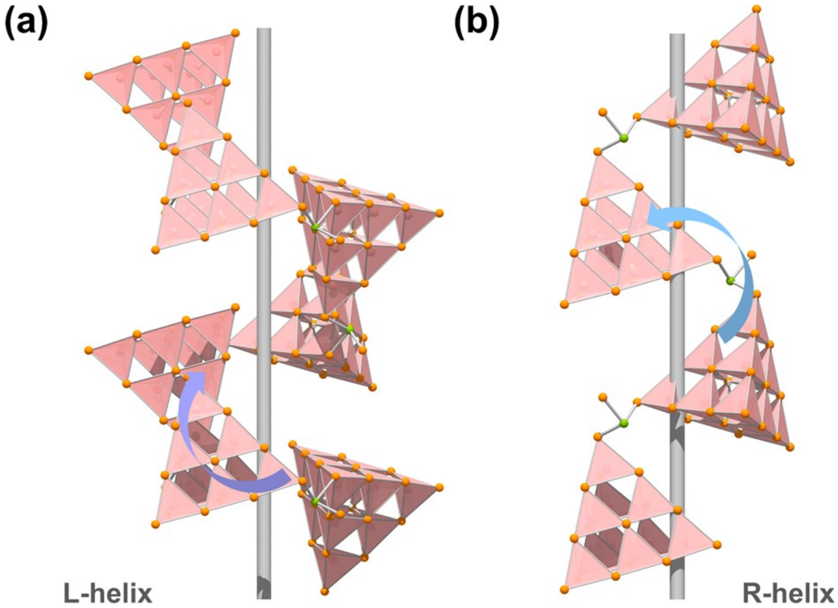

Figure S3. View of (a) 1D left-handed helix (L-helix) and (b) right-handed helix (R-helix) of **NCF-3** along the *a* axis.

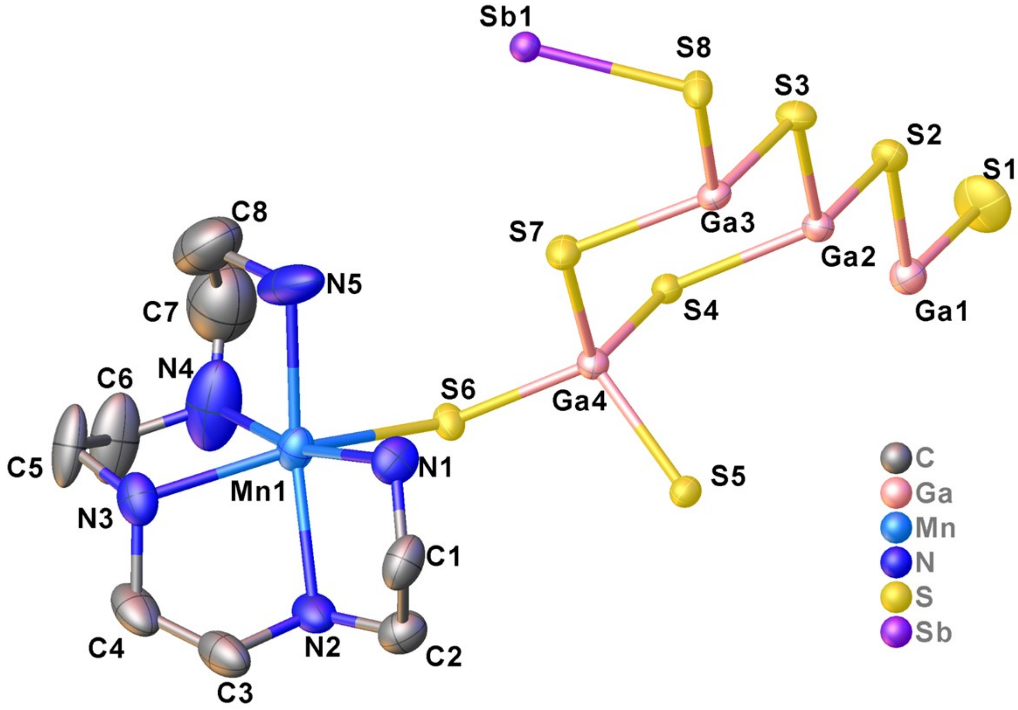

Figure S4. The asymmetric unit of **NCF-3-Mn** with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

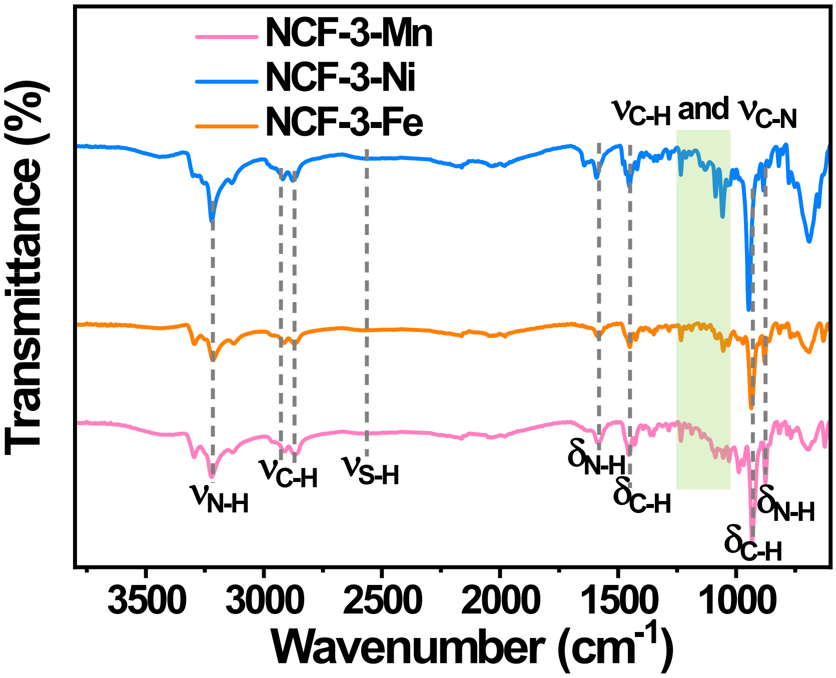

Figure S5. FT-IR spectrums of **NCF-3**.

The peaks at about 3220 cm^{-1}, 2912 cm^{-1} and 2868 cm^{-1} belong to the stretching vibration of N-H and C-H of TEPA, respectively. The peaks at 1250 ~ 1030 cm^{-1} are for the stretching vibration of C-N and C-C of TEPA. The peaks at 1454 cm^{-1} and 931 cm^{-1} belong to the bending vibration of C-H of TEPA, while the peaks at 1583 cm^{-1} and 875 cm^{-1} belong to the bending vibration of N-H of TEPA. To be noted, the weak and broad peak at 2564 cm^{-1} is assigned to the S-H stretching vibration of S-H according to the literatures.[1-3]

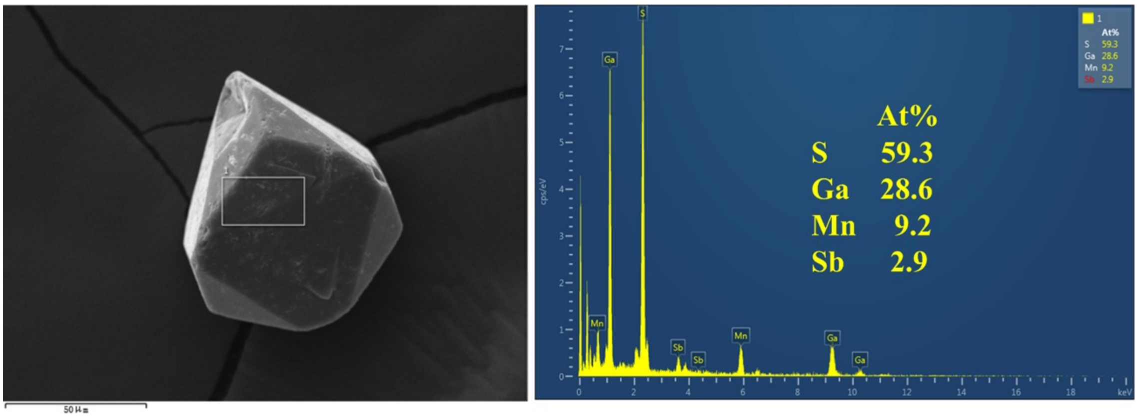

Figure S6. Left: SEM image of as-synthesized **NCF-3-Mn**. Right: EDS of **NCF-3-Mn**.

The results clearly confirmed the presence of Mn, Ga, Sb and S elements, and the measured molar ratio of Mn/Ga/Sb/S is 3.17:9.86:1:20.45, which is consistent with the theoretical value of 3:10:1:20.

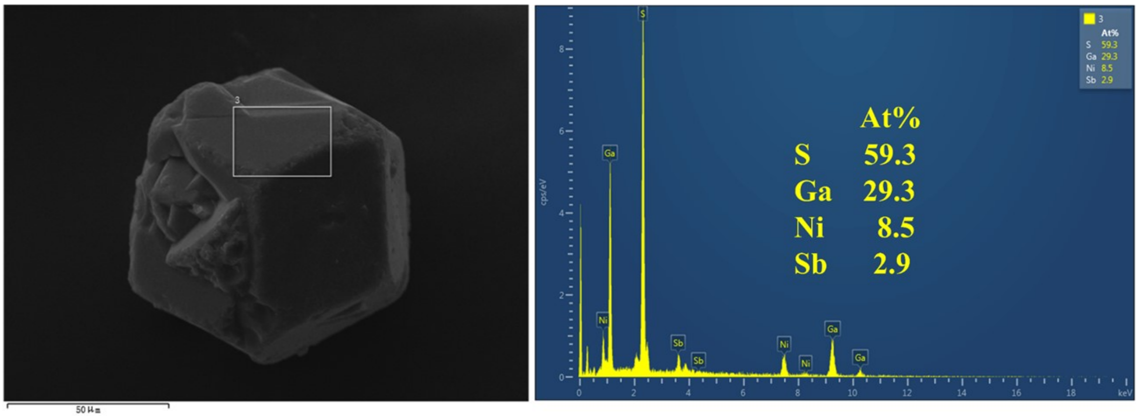

Figure S7. Left: SEM image of as-synthesized **NCF-3-Ni**. Right: EDS of **NCF-3-Ni**.

The results clearly confirmed the presence of Ni, Ga, Sb and S elements, and the measured molar ratio of Ni/Ga/Sb/S is 2.93:10.10:1:20.45, which is consistent with the theoretical value of 3:10:1:20.

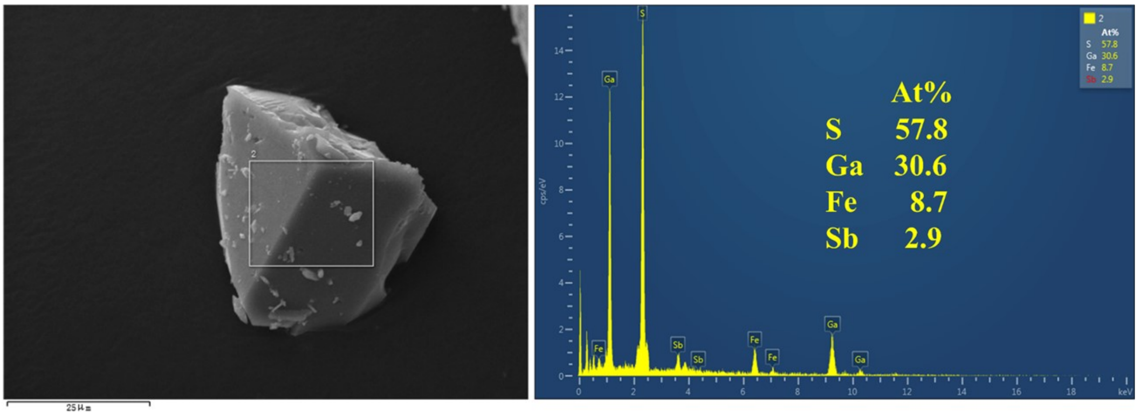

Figure S8. Left: SEM image of as-synthesized **NCF-3-Fe**. Right: EDS of **NCF-3-Fe**.

The results clearly confirmed the presence of Fe, Ga, Sb and S elements, and the measured molar ratio of Fe/Ga/Sb/S is 3.00:10.55:1:19.93, which is consistent with the theoretical value of 3:10:1:20.

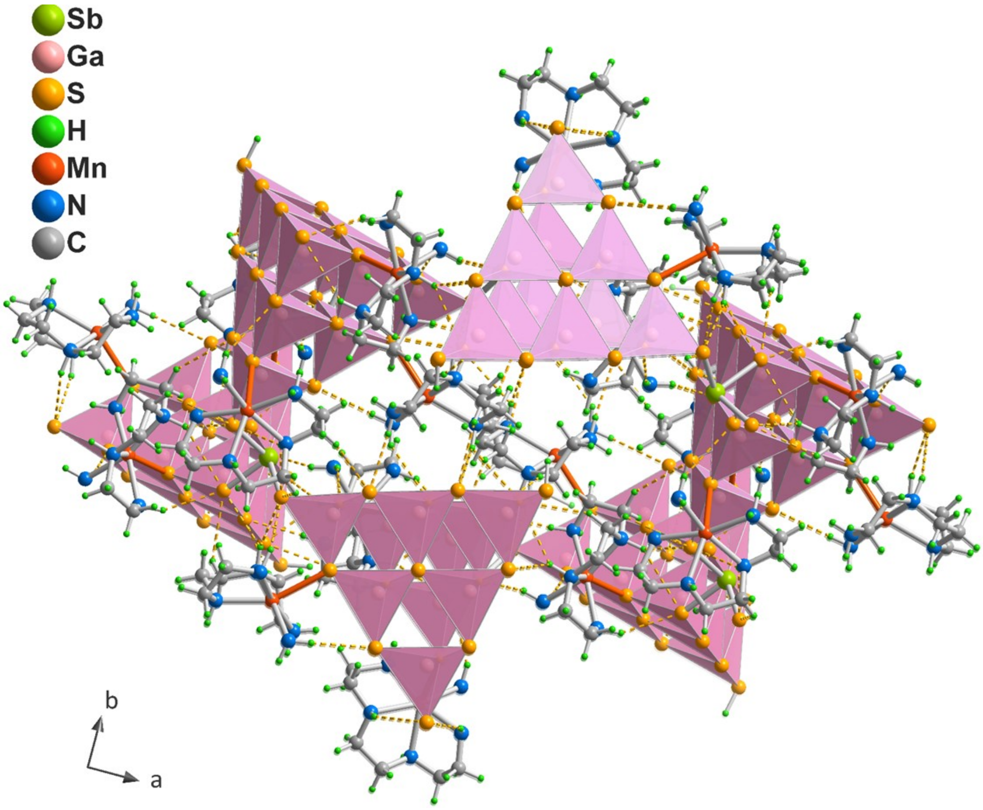

Figure S9. Part of the crystal structure of NCF-3-Mn, showing the formation of interconnecting N/C–H···S H-bonds (yellow dashed lines) within the pore of framework.

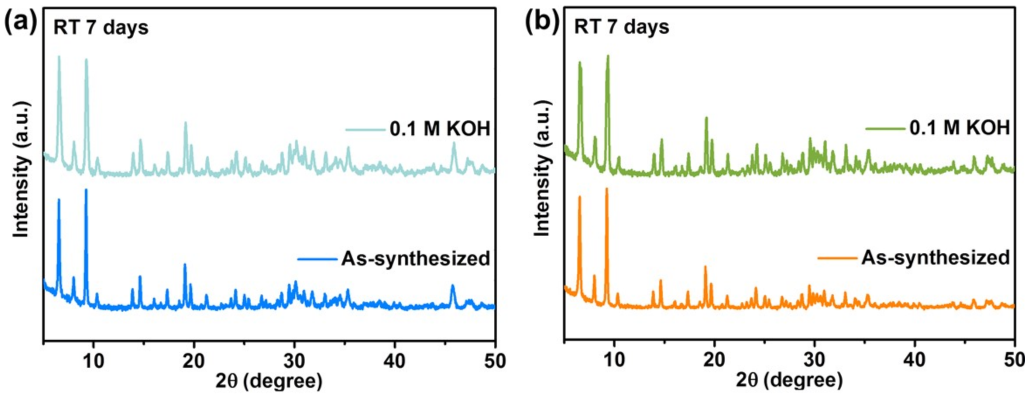

Figure S10. PXRD patterns of (a) **NCF-3-Ni** and (b) **NCF-3-Fe** after immersion in 0.1 M KOH at room-temperature (RT) for 7 days.

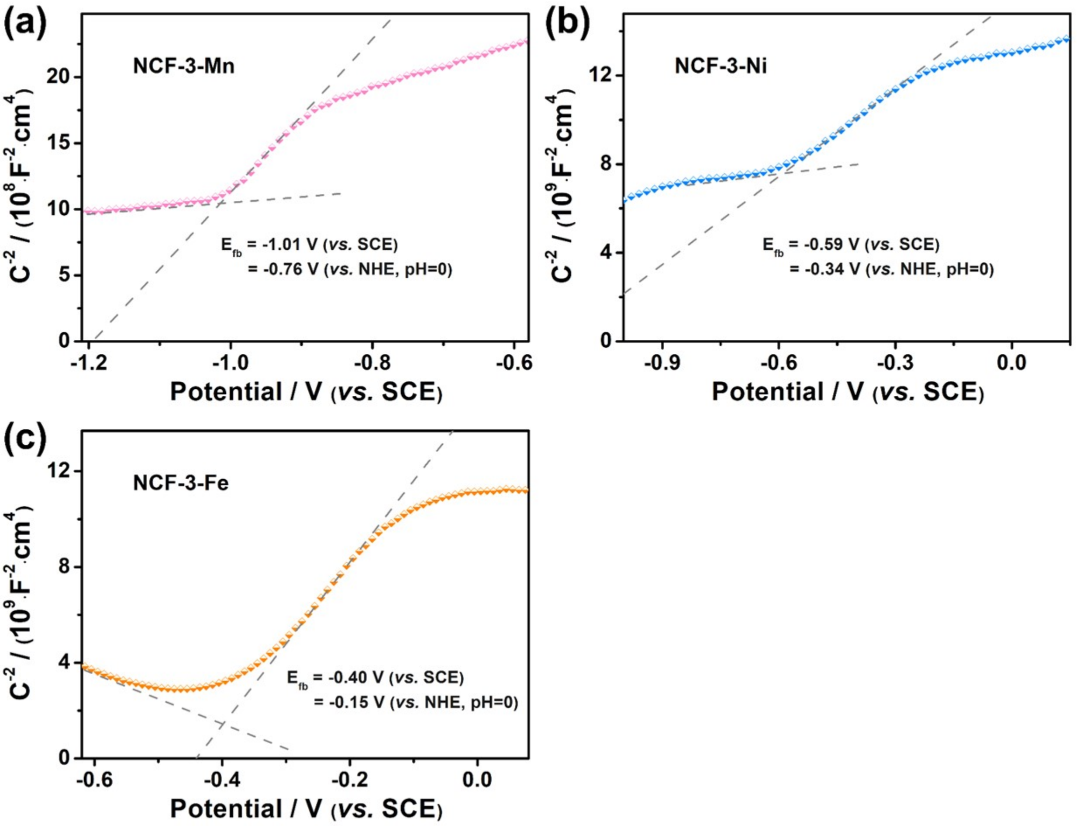

Figure S11. Mott-Schottky plots (1500Hz)of (a) **NCF-3-Mn**, (b) **NCF-3-Ni** and (c) **NCF-3-Fe**.

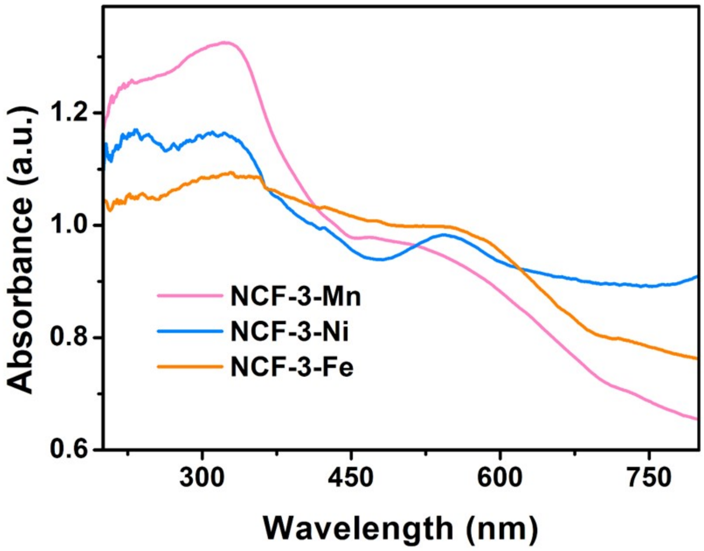

Figure S12. UV-vis absorption spectra of **NCF-3-Mn**, **NCF-3-Ni** and **NCF-3-Fe.**

Table S1. Crystallographic and structure refinement data of **NCF-3-Mn**, **NCF-3-Ni** and **NCF-3-Fe**.

Compound	**NCF-3-Mn**	**NCF-3-Ni**	**NCF-3-Fe**
Empirical formula	$Mn_3Ga_{10}SbS_{20}C_{24}N_{15}H_{70}\cdot xH_2O$	$Ni_3Ga_{10}SbS_{20}C_{24}N_{15}H_{70}\cdot xH_2O$	$Fe_3Ga_{10}SbS_{20}C_{24}N_{15}H_{70}\cdot xH_2O$
Crystal system	cubic	cubic	cubic
Z	4	4	4
Space group	$P2_13$	$P2_13$	$P2_13$
a (Å)	19.1330(4)	19.1266(9)	19.1091(9)
α (deg)	90	90	90
V (Å^3)	7004.1(4)	6997.0(10)	6977.8(10)
F (000)	4300.0	4376.0	4312.0
T (K)	120 K	120 K	120 K
D (g cm^{-3})	2.081	2.110	2.091
μ (mm^{-1})	5.307	5.581	5.408
Collected reflections	53185	32138	55168
Independent reflections	5163	4290	4280
Flack parameter	0.014(5)	0.420(11)	0.025(19)
GOF on F^2	1.126	1.054	1.046
R_1, wR_2 ($I>2\sigma(I)$)	0.0352, 0.0882	0.0213, 0.0452	0.0325, 0.0712
R_1, wR_2 (all data)	0.0452, 0.0981	0.0258, 0.0472	0.0423, 0.0759

References

1 Y.-H. Wang, M.-H. Zhang, Y.-M. Yan, G.-Q. Bian, Q.-Y. Zhu and J. Dai, *Inorg. Chem.*, 2010, **49**, 9731.

2 J. L. Mertz, N. Ding and M. G. Kanatzidis, *Inorg. Chem.*, 2009, **48**, 10898-10900.

3 J. Zhou, Y. Zhang, G.-Q. Bian, C.-Y. Li, X.-X. Chen and J. Dai, *Cryst. Growth Des.*, 2008, **8**, 2235-2240.